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# Decay resistance and dimensional stability of *Araucaria angustifolia* using siloxanes synthesized by sol–gel process

Carlos A. Giudice [a,b,*], Paula V. Alfieri [b], Guadalupe Canosa [a]

[a] UTN (Universidad Tecnológica Nacional), Calle 60 y 124, 1900 La Plata, Argentina
[b] CIDEPINT (Centro de Investigación y Desarrollo en Tecnología de Pinturas), Calle 52 e/121 y 122, 1900 La Plata, Argentina

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ABSTRACT

Solid wood specimens of *Araucaria angustifolia* were impregnated with alkoxysilanes hydrolyzed and condensed "in situ" by the sol–gel process. Alkoxysilanes selected were *aminopropyl methyldiethoxysilane* and *aminopropyl triethoxysilane*; it was also used the aminopropyl *methyldiethoxysilane*/*aminopropyl triethoxysilane* mixture in 50/50 ratio w/w. The pH was adjusted to alkaline value for controlling kinetic of hydrolysis and condensation reactions.

Impregnation process was carried out under controlled operating conditions to achieve different weight gains of the chemical modifier.

Unmodified and modified wood specimens were exposed to brown rot (*Polyporus meliae*) and white rot (*Coriolus versicolor)* under laboratory conditions.

The results indicate that the improved resistance to fungal exposure would be based on the wood chemical modification (the protection of cellulose caused by steric hindrance of ≡Si–O–Cellulose preventing the formation of enzyme–substrate complex). Moreover, the results also would be based on the enhanced dimensional stability of the treated wood; the quoted high dimensional stability, which limits the growth of the spores, is supported in the hydrophobicity generated by both the decreasing of the amount of polar hydroxyl groups and the partial occupation of pores with polysiloxanes.



## 1. Introduction

The civil and industrial use of wood requires pretreatment and maintenance for controlling its biodeterioration.

Microorganisms have the carbon as the main cell constituent; they obtain it from various sources (Brock and Madigan, 1991; Lynd et al., 2002; Murashima et al., 2002). There is a great diversity of microorganisms; thus, for example, aerobic or anaerobic bacteria and fungi using cellulose, hemicellulose and lignin of wood as carbon source (Ramírez and Coha, 2003). This metabolic variety makes very difficult to control the attack or growth on any substrate since they have the ability to adapt their metabolism to environmental conditions, even when they are extreme.

The microbial attack consists in the enzymatic catalysis of hydrolysis of the β-1,4 glucosidic bonds of cellulose. It is produced by an endonuclease (EC 3.2.1.4), which hydrolyzes bonds providing separate units of glucose, cellobiose and cellodextrins; the last interrupts the supramolecular aggregate and increasing reduction of the end groups. Enzymatic hydrolysis of cellulose has been extensively investigated from lot of years ago by many authors; therefore, the chemical changes occurring in decayed wood are well known (Focher et al., 1991; Walker and Wilson, 1991; Bhatawdekar et al., 1992; Covaco et al., 1998; Papadopoulos and Hill, 2002; Papadopoulos et al., 2010).

The bibliographic information mentions that a minimum concentration of cellulase (about $3 \times 10^{-5}$ units/ml) can generate a significant carbon loss from all cellulose sources in only two days (Schulein, 1997).

One of the most used pretreatments is thermal modification of wood. This method is knowingly beneficial since it changes dimensional stability, hygroscopicity and decay resistance of the wood (Tjeerdsma and Militz, 2005; Boonstra and Tjeerdsma, 2006; Boonstra et al., 2007; Militz, 2008; Karlsson et al., 2011).

Beyond the scientific and technological advances reached in thermal treatments, the chemical modification of wood is also a very used method (Norimoto, 2001; Saka et al., 2001; Sebe and Brook, 2001; Tshabalala et al., 2003; Donnath et al., 2004; Hill et al., 2004; Mai and Militz, 2004; Sebe et al., 2004; Yamaguchi, 2005; Nami Kartal et al., 2007). Commercially available chemicals used to modify the wood usually include anhydrides, isocyanates,

* Corresponding author. UTN (Universidad Tecnológica Nacional), Calle 60 y 124, 1900 La Plata, Argentina. Tel.: +54 221 155440384; fax: +54 221 427 1537.
*E-mail address:* cagiudice@yahoo.com (C.A. Giudice).

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chlorides, lactones, nitriles, epoxies, etc (Rowell, 1983, 2005, 2006; Kumar, 1994; Chang and Chang, 2006).

The chemical modification is based on the well-known reaction between hydroxyl groups of cellulose, hemicellulose and lignin with different reagents, which should be selected according to the desired properties (decay resistance, dimensional stability, fire resistance, etc.). It should be mentioned that the modification by reaction of only a hydroxyl group of glycoside ring leads to the protection of the cellulose from enzymatic attack (Teeri and Koivula, 1995; Levy et al., 2002).

Nevertheless, despite the progress made, it is interesting to continue studies involving chemical modification of any type and specie of wood through the reaction of the hydroxyl groups by using modern environmentally friendly materials of low cost and easy impregnation and curing inside wood pores.

In this study, investigations were developed to establish the properties of chemically modified wood by impregnation with alkoxysilanes hydrolyzed and condensed "in situ" by the sol–gel process, in order to permit the preservation against microorganism attack.

## 2. Materials and methods

### 2.1. Cellulose activation

Considering the anatomical structure of wood, the cell wall has a chemical composition quite heterogeneous. It basically consists of three polymeric materials (cellulose, hemicellulose and lignin) in 95–98% w/w; the distribution of these three polymeric materials along the cell wall is not uniform and depends on the specie. The remainder is composed of low molecular weight compounds known as extractives; this term includes a wide variety of chemical compounds, such as terpenes and related products, fatty acids, aromatic compounds and volatile oils.

The hydroxyl groups of the lignin have high reactivity to chemical agents while in the case of those present in the cellulose, the accessibility (reactivity) depends substantially on whether its structure is crystalline or amorphous.

The above bases the previous activation of the cellulose. The latter can be achieved by treatment with hot water or aqueous solutions, which is associated with the swelling of cellulose. Although various methods have been developed (i.e. enzymes, controlled microorganisms, etc.), the use of alkaline solutions of sodium hydroxide is still widely used. For this reason, this activation method was selected in this experiment.

During activation of the cellulose, the crystalline form changes from cellulose I (native) to cellulose II (reduction of molecular packing and alteration of hydrogen bridges distribution and exposed glycosidic bonds); in addition, it is generally observed a partial removal of hemicellulose and lignin.

### 2.2. Sol-gel process

It involves the hydrolysis and condensation reactions of metal-organic precursors. In the case of silicon, the above reactions are as follows:

$$\equiv Si{-}O{-}R + H_2O \leftrightarrow \equiv Si{-}OH + R{-}OH$$
Hydrolysis

$$\equiv Si{-}O{-}R + HO{-}Si\equiv \leftrightarrow \equiv Si{-}O{-}Si\equiv + R{-}OH$$
Condensation of alcohol

$$\equiv Si{-}OH + HO{-}Si\equiv \leftrightarrow \equiv Si{-}O{-}Si\equiv + H_2O$$
Condensation of water

In this process, the pH of the solution is an important variable for the influence exerting on the polymerization kinetic. In acid catalysis (pH below the isoelectric point), hydrolysis and condensation rates are rapid (low sol stability and consequently reduced gel time). In basic catalysis (strongly alkaline pH), the hydrolysis rate is also relatively fast but condensation reaction is low, resulting in a decrease in the overall speed of the reaction (enhanced sol stability and therefore increased gel time).

To prepare high-density gels, it is not recommended a high kinetic of hydrolysis and condensation reactions since many ≡Si–OH and/or ≡Si–OR groups may remain trapped (difficult condensation due to steric hindrance). In this experiment and taking into account the above, it was considered convenient to select an alkaline medium.

The hydrolysis and condensation reactions lead to the formation of aggregates (clusters), which are then linked to form a single large aggregate called gel. After gelation, the system continues producing nanostructural and chemical changes (aging). At this stage, the polymerization reactions continue increasing the links ≡Si–O–Si≡.

Simultaneously to the aforementioned reactions, the wood chemical modification also occurs. This chemical modification, which involves the reaction of hydroxyl groups, was studied by many researchers (Devi et al., 2004; Chang and Chang, 2006; Hill, 2006; Rowell, 2006; Pandey et al., 2009; Papadopoulos et al., 2010; Sonowal and Gogoi, 2010; Wu et al., 2012).

The bonds ≡Si–O–C≡ would arise from hydrolysis of alkoxides and the subsequent condensation of ≡Si–OH with the –OH of the wood according to reaction:

$$\equiv Si{-}OH + HO{-}Cellulose\equiv \leftrightarrow \equiv Si{-}O{-}Cellulose\equiv + H_2O$$
Condensation of water

Fig. 1 shows a schematic representation of the chemical reaction that would take place between wood and polysiloxanes. The ≡Si–OH is initially assembled to the –OH of wood via hydrogen bond; then, water is removed and covalent bonds are formed (Liu et al., 2011).

Finally, during the evolution of the reactions of hydrolysis and condensation and even after their completion, the system contraction takes place because of the expulsion of the liquid phase contained in the wood pores (water and alcohol); this leads to hardening of the gel (xerogel).

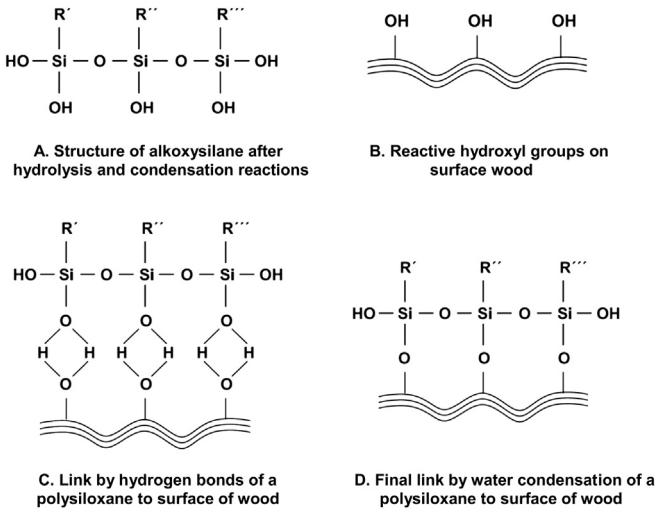


**Fig. 1.** Schematic representation of the chemical reaction taking place between polysiloxanes and wood.

Owing to that a rapid aging could lead to fracture of the gel, in this experiment solid wood specimens were exposed under controlled laboratory conditions for allowing the gelation (hydrolysis and condensation reactions) and aging (natural drying).

The experiment included (i) preparation of specimens of *Araucaria angustifolia* for tests, (ii) selection of wood modifying reagents and operating conditions of impregnation, and finally (iii) laboratory tests.

### 2.3. Preparation of specimens of Araucaria angustifolia for tests

Specimens of *Araucaria angustifolia* (common names, pino Paraná and pino Brasil), free of defects, were prepared for each test with 20 × 20 × 20 mm size.

In a first stage, the specimens were pretreated in a Soxhlet extractor for 2 h with a solution of sodium hydroxide (pH 8.5) and then for about 5 min with distilled water to remove the alkali remaining on surface. Subsequently, the specimens were exposed in a chamber under controlled temperature and humidity conditions (20 ± 2 °C and 60 ± 5% RH) until reaching the equilibrium moisture according to the guidelines of ASTM D 4933.

### 2.4. Selection of wood modifying reagents and operating conditions of impregnation

#### 2.4.1. Wood modifying reagents

Alkoxysilanes were selected as wood reactive modifiers. They were *aminopropyl methyldiethoxysilane* (chemical formula, $C_8H_{21}NO_2Si$; molecular weight, 191.3; aspect, clear liquid; density, 0.916 g $cm^{-3}$) and the *aminopropyl triethoxysilane* (chemical formula $C_9H_{23}NO_3Si$, molecular weight 221.4; aspect, clear liquid; density, 0.956 g $cm^{-3}$); in the research, it was also used the aminopropyl *methyldiethoxysilane*/*aminopropyl triethoxysilane* mixture in 50/50 ratio w/w.

In the present experiment, ethanol was used as solvent in 4/1 ethanol/alkoxide molar ratio; it is noteworthy that the alcohol (product of hydrolysis and condensation reactions) is not only a solvent since its molecular weight regulates the speed of evaporation and consequently the kinetics of sol–gel process (reversible reactions).

As quoted, the pH was adjusted to alkaline value for controlling kinetic of hydrolysis and condensation reactions; for it, ammonium hydroxide (conc.) was used until reaching pH 8.2 ± 0.1. Amino groups from alkoxides collaborate with the alkalinity.

It is worth mentioning that the selected alkoxides exhibit low toxicity and are not polluting to the environment.

#### 2.4.2. Conditions of impregnation

Concerning impregnation process, this was carried out at 45–50 °C in an autoclave equipped with vacuum pump and compressor, under controlled operating conditions. In all cases, the 3/1 impregnant solution/wood v/v ratio was selected to ensure that the wood specimens were completely submerged during the entire process. Then, the autoclave was charged with the pretreated wood specimens and it was applied a vacuum of 200 mm Hg for 10 min to release air and water vapor from the cells to facilitate the penetration of chemical modifier.

Later, the corresponding alkoxide solution was added without decreasing the vacuum level. The operating conditions were adjusted to achieve different weight gains of the chemical modifier: the pressure was gradually increased from 1.5 to 6.5 kg $cm^{-2}$ to facilitate the penetration; this stage lasted from 15 to 120 min. The next one was the application of a slight vacuum (about 50 mm Hg for 10 min) to remove the excess alkoxide on the wood specimens surface.

Finally, the wood specimens were removed after reaching atmospheric pressure; later, they were exposed into a chamber under controlled temperature and humidity conditions (20 ± 2 °C and 60 ± 5% RH) for three weeks for allowing the gelation and aging.

Weight percent gain was determined by using the equation $WPG = [(Wm - Wo)/Wo] \times 100$, where Wo and Wm are the weight of the wood specimens pretreated in the Soxhlet and the weight of those chemically modified in the autoclave, respectively (all of which were previously dried in an oven at 100 ± 3 °C up to constant weight).

### 2.5. Laboratory tests

#### 2.5.1. Dimensional stability

The degree of dimensional stability was determined by estimating the Volumetric Swelling Coefficient S and the Anti-Swell Efficiency ASE (Devi et al., 2004; Pandey et al., 2009).

The saturation water was evaluated using the ASTM D 4442. The specimens were immersed in distilled water at 20 ± 2 °C up to constant weight; then, the specimens were removed, the excess water was drained and the volume of specimens was determined by the mercury displacement method. Finally, the specimens were dried in oven at 100 ± 3 °C and the volume was again quantified by the aforementioned method.

Finally, the Volumetric Swelling Coefficient was calculated by using the equation $S, \% = 100\ (V2 - V1)/V1$, where V2 and V1 are the volumes of saturated and oven dried specimens, respectively.

Concerning Anti-Swell Efficiency, it was calculated by using the expression $ASE, \% = 100\ (Ss - Sm)/Ss$, where Ss and Sm are the average expansion coefficients of the unmodified and modified specimens, respectively.

Finally, the immersion process was repeated at 20 ± 2 °C in distilled water for 72 h in order to determine the leachability of the cured impregnant through the S and ASE values in a second cycle.

#### 2.5.2. Decay resistance

All the specimens of *Araucaria angustifolia* were exposed, under laboratory conditions, to *Polyporus meliae* (brown rot) and *Coriolus versicolor* (white rot), following the general guidelines of ASTM D 2017. The specimens were previously sterilized in an autoclave and then exposed in culture flasks to the action of quoted fungi on 3% malt extract agar; the flasks were inoculated one week before beginning the test.

The specimens, prepared on glass rods for avoiding direct contact with the culture medium, were maintained for 12 weeks under controlled conditions (25 ± 5 °C and 60–70% RH).

Then, the specimens were removed from the culture flasks and sterilized again; mycelia were subsequently withdrawn. Finally, the specimens were placed in an oven at 100 ± 3 °C up to constant weight. Weight loss was determined for each specimen by using the following equation $WL, \% = [(Wo - Wf)/Wo] \times 100$, where Wo and Wf are the weight of the dried specimens without and with exposure to fungi, respectively.

## 3. Results and discussions

Table 1 displays specimen identification and the weight gain after alkoxide gelation and subsequent drying of wood specimens.

### 3.1. Dimensional stability of modified wood

In the first stage, the values of S and ASE were calculated for both cycles of immersion in distilled water.

The average results of S and the standard deviations are listed in Table 2. The values for unmodified specimens were similar for the

**Table 1**
Weight percent gain and standard deviation of modified wood specimens.

| Alkoxide | WPG | Specimen |
|---|---|---|
| A, aminopropyl methyldiethoxysilane | 2.28 (0.38) | A.I |
| | 6.03 (0.29) | A.II |
| | 9.89 (0.43) | A.III |
| | 12.98 (0.68) | A.IV |
| | 16.21 (0.99) | A.V |
| | 19.42 (1.01) | A.VI |
| B, aminopropyl triethoxysilane | 2.61 (0.28) | B.I |
| | 6.45 (0.33) | B.II |
| | 10.05 (0.43) | B.III |
| | 13.63 (0.55) | B.IV |
| | 16.62 (0.39) | B.V |
| | 18.75 (0.66) | B.VI |
| C, aminopropyl methyldiethoxysilane/ aminopropyl triethoxysilane (50/50 w/w) | 2.80 (0.24) | C.I |
| | 6.61 (0.36) | C.II |
| | 10.33 (0.46) | C.III |
| | 13.42 (0.68) | C.IV |
| | 16.78 (0.55) | C.V |
| | 20.02 (0.78) | C.VI |
| D, control | 0.00 | D |

first and second cycles of immersion; it would be based on that extractives were removed in a previous stage.

After finishing the three modifications of the specimens with alkoxides A, B and C (Table 1), it is observed that values of S decreased significantly as the modification degree increased (weight gain of alkoxides hydrolyzed and condensed inside the wood pores).

For comparison, Table 2 includes the average values for specimens modified with each alkoxide for both cycles of immersion in distilled water. It is concluded that there was less volumetric expansion in those treated with the alkoxide B, then with C and finally with A, for all weight gains considered. The different reactivity of the alkoxides and therefore the dissimilar modification degree of the wood components would base the results obtained.

Furthermore, it is important to explicit the S average values obtained with the alkoxide B cured inside the wood: 2.74 and 2.78% (weight gain, 18.75%) for the first and second cycles of immersion, respectively. The similar values in both cycles indicate the high insolubility of the cured alkoxide.

The very small volumetric expansion due to water absorption up to saturation point of fibers, which indicates a high hydrophobicity of the wood after modification (low content of the equilibrium moisture), could be attributed to the partial occupation of pores by siloxanes and fundamentally to the interaction of reactive alkoxides with cell wall components.

With regard to ASE (Table 2), the average values denote a significant dependence on the modification degree; they increased as weight gain increased. Values of ASE for the modified wood corroborated values of S.

### 3.2. Decay resistance

Table 2 also displays a significant reduction in weight loss of the modified specimens in relation to the unmodified ones after 12 weeks of exposure to *Polyporus meliae* and *Coriolus versicolor*. Thus, for the modifier B, a weight loss of only 2.87 and 6.78% was achieved; these values are significantly lower than those presented by the control specimen (43.28 and 31.63% for the brown rot and white rot, respectively).

For all weight gains recorded in the chemical modification of wood, the lowest weight loss was registered with specimens modified with alkoxide B, then with the C and finally with the A; in all cases, greater weight gain led to a better performance. The average values for each modifier corroborate the above mentioned.

It is important to make explicit the very low final values achieved with the alkoxide B: 0.22% and 0.60% (for the greatest weight gain in chemically modified specimens) respectively for *Coriolus versicolor* and *Polyporus meliae*.

The results indicate that the improved resistance to fungal exposure would be based on the wood chemical modification (the protection of cellulose caused by steric hindrance of ≡Si–O–Cellulose preventing the formation of enzyme–substrate complex).

**Table 2**
Dimensional stability and weight loss of modified wood specimens.

| Specimen | Dimensional stability | | | | Weight loss, % | |
|---|---|---|---|---|---|---|
| | S, % | | ASE, % | | *Polyporus meliae* | *Coriolus versicolor* |
| | 1st cycle | 2nd cycle | 1st cycle | 2nd cycle | | |
| A.I | 7.09 (0.98) | 7.03 (1.00) | 36.86 | 37.29 | 15.88 (1.11) | 24.68 (1.48) |
| A.II | 5.99 (0.92) | 6.00 (0.93) | 46.66 | 46.48 | 2.65 (0.21) | 13.25 (0.93) |
| A.III | 5.06 (0.42) | 5.07 (0.43) | 54.94 | 54.77 | 1.71 (0.12) | 6.85 (0.48) |
| A.IV | 4.49 (0.39) | 4.47 (0.40) | 60.02 | 60.12 | 0.69 (0.05) | 3.66 (0.29) |
| A.V | 3.91 (0.15) | 3.87 (0.19) | 65.18 | 65.48 | 0.34 (0.01) | 1.63 (0.09) |
| A.VI | 3.39 (0.15) | 3.37 (0.11) | 69.81 | 69.94 | 0.28 (0.01) | 0.78 (0.03) |
| Average value | 4.99 | 4.97 | 55.58 | 55.68 | 3.59 | 8.48 |
| B.I | 5.74 (0.98) | 5.87 (0.91) | 48.89 | 47.64 | 12.70 (1.01) | 19.68 (1.47) |
| B.II | 4.73 (0.48) | 4.61 (0.52) | 57.88 | 58.88 | 2.12 (0.17) | 10.73 (0.75) |
| B.III | 4.03 (0.28) | 4.14 (0.31) | 64.11 | 63.07 | 1.37 (0.08) | 5.34 (0.37) |
| B.IV | 3.58 (0.18) | 3.48 (0.21) | 68.12 | 68.96 | 0.55 (0.03) | 3.03 (0.21) |
| B.V | 3.13 (0.13) | 3.08 (0.15) | 72.13 | 72.52 | 0.27 (0.01) | 1.30 (0.09) |
| B.VI | 2.74 (0.16) | 2.78 (0.13) | 75.60 | 75.20 | 0.22 (0.01) | 0.60 (0.03) |
| Average value | 3.99 | 3.99 | 64.46 | 64.38 | 2.87 | 6.78 |
| C.I | 6.38 (0.99) | 6.26 (0.93) | 43.19 | 44.16 | 14.22 (0.99) | 22.31 (1.56) |
| C.II | 5.45 (0.69) | 5.39 (0.60) | 51.47 | 51.92 | 2.43 (0.17) | 12.32 (0.86) |
| C.III | 4.55 (0.45) | 4.56 (0.40) | 59.48 | 59.32 | 1.49 (0.10) | 6.03 (0.42) |
| C.IV | 3.95 (0.28) | 3.98 (0.36) | 64.83 | 64.50 | 0.62 (0.04) | 3.26 (0.23) |
| C.V | 3.52 (0.21) | 3.48 (0.14) | 68.66 | 68.96 | 0.31 (0.02) | 1.48 (0.10) |
| C.VI | 3.05 (0.18) | 3.03 (0.21) | 72.84 | 72.97 | 0.24 (0.01) | 0.69 (0.05) |
| Average value | 4.48 | 4.45 | 60.08 | 60.30 | 3.22 | 7.68 |
| D | 11.23 (1.13) | 11.21 (1.19) | – | – | 43.28 (3.03) | 31.63 (2.21) |

Moreover, the results also would be based on the enhanced dimensional stability of the treated wood (reduced Volumetric Coefficient Swelling S and elevated Anti-Swell Efficiency ASE). The quoted high dimensional stability, which limits the growth of the spores, is supported in the hydrophobicity generated by both the decreasing of the amount of polar hydroxyl groups of unmodified wood due to condensation reactions with low polarity alkoxides used in the treatment of impregnation and the partial occupation of pores with polysiloxanes formed by sol–gel process.

## 4. Conclusions

- Polysiloxanes synthesized inside the wood pores by the sol–gel process, by using *aminopropyl methyldiethoxysilane*, *aminopropyl triethoxysilane and* aminopropyl *methyldiethoxysilane*/*aminopropyl triethoxysilane* mixture in 50/50 ratio w/w as precursors, proved to be efficient for controlling the decay resistance and improving the dimensional stability of *Araucaria angustifolia*.
- The results indicate that the best performance was observed with woods treated with aminopropyl triethoxysilane, followed by those modified with a mixture of both alkoxides and with aminopropyl methyldiethoxysilane, in this order; the different reactivity of the alkoxides and therefore the dissimilar modification degree of the wood components would base the results obtained.
- For all chemical treatments, the decay resistance and dimensional stability increased significantly with the modification degree (weight gain of alkoxides hydrolyzed and condensed inside the wood pores); technical and economic studies should define the most appropriate level for each condition of use of the modified wood.

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